

Characterization of individual aerosol particles associated with clouds (CRYSTAL-FACE*)

****Cirrus Regional Study of Tropical Anvils and Cirrus Layers -
Florida Area Cirrus Experiment***

Final Report

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The aim of our research was to obtain data on the chemical and physical properties of individual aerosol particles from near the bottoms and tops of the deep convective systems that lead to the generation of tropical cirrus clouds and to provide insights into the particles that serve as CCN or IN. We used analytical transmission electron microscopy (ATEM), including energy-dispersive X-ray spectrometry (EDS) and electron energy-loss spectroscopy (EELS), and field-emission electron microscopy (FESEM) to compare the compositions, concentrations, size distributions, shapes, surface coatings, and degrees of aggregation of individual particles from cloud bases and the anvils near the tropopause.

Aggregates of sea salt and mineral dust, ammonium sulfate, and soot particles are abundant in in-cloud samples. Cirrus samples contain many H₂SO₄ droplets, but acidic sulfate particles are rare at the cloud bases. H₂SO₄ probably formed at higher altitudes through oxidation of SO₂ in cloud droplets. The relatively high extent of ammoniation in the upper troposphere in-cloud samples appears to have resulted from vertical transport by strong convection. The morphology of H₂SO₄ droplets indicates that they had been at least partly ammoniated at the time of collection. They are internally mixed with organic materials, metal sulfates, and solid particles of various compositions. Ammoniation and internal mixing of H₂SO₄ in the upper troposphere aerosols may result in freezing at higher temperature than in pure H₂SO₄ aerosols. K- and S-bearing organic particles and Si-Al-rich particles are common throughout. Sea salt and mineral dust were incorporated into the convective systems from the cloud bases and worked as ice nuclei while being vertically transported. The nonsulfate particles originated from

the lower troposphere and were transported to the upper troposphere and lower stratosphere.

Papers

1. Kojima, T., Buseck, P.R., Wilson, J.C., Reeves, J.M., and Mahoney, M.J. (2004) Aerosol particles from tropical convective systems: Cloud tops and cirrus anvils. *Journal of Geophysical Research-Atmospheres* **109**, doi:10.1029/2003JD004504.
2. Kojima, T., Buseck, P.R., and Reeves, J.M. (2005) Aerosol particles from tropical convective systems: Cloud bases. *Journal of Geophysical Research-Atmospheres* **109**, in press.
3. Murphy, D.M., Cziczo, D.J., Hudson, P.K., Thomson, D.S., Wilson, J.C., Kojima, T., and Buseck, P.R. (2004) Particle generation and resuspension in aircraft inlets when flying in clouds. *Aerosol Science and Technology* **38**, 400-408.

Oral Presentations

4. Buseck, P.R., Friedrich, H., Kojima, T., and Spinsby, J. (2004) Nanoparticles in the troposphere, 227th Am. Chem. Soc. Natl. Mtg., Anaheim, CA. *ACS Abstrs.*, Abstr. I&EC 40, March, 2004.
5. Kojima, T., Buseck, P.R., and Reeves, J.M. (2003) Comparison of aerosol particles collected from cloud bases and cirrus anvils, Am. Geophys. Union Fall Mtg., San Francisco, CA (*Eos, Trans. AGU* **84** (46) Fall Meet. Suppl., Abstr. A12D-08, December, 2003.
6. Kojima, T., Buseck, P.R., Wilson, J.C., and Reeves, J.M. (2003) TEM analysis of aerosol particles and its application to cloud formation and climate, 2003 Symp. on "Recent Developments and Applications of Atomic Resolution Electron Microscopy and Spectroscopy – a Silver Jubilee," Tempe, AZ, ASU. *Prog. & Abstr.*, January, 2003.
7. Kojima, T., Buseck, P.R., Wilson, J.C., and Reeves, J.M. (2002) Aerosol particles from tropical cirrus clouds in the lower stratosphere: Am. Geophys. Union Fall Mtg., San Francisco, CA. *Eos, Trans. AGU* **83** (47) Fall Meet. Suppl., F106, Abstr. A71F-06, December, 2002.

Abstracts of papers

1. Kojima, T., Buseck, P.R., and Reeves, J.M. (2005) Aerosol particles from tropical convective systems: Cloud bases. *Journal of Geophysical Research-Atmospheres* **109**, in press.

Aerosol particles collected from cloud bases during the Cirrus Regional Study of Tropical Anvils and Cirrus Layers-Florida Area Cirrus Experiment (CRYSTAL-FACE) consist of ammonium sulfate (45-90 % by number), sea salt (5-45 %), mineral dust (1-20 %), and anthropogenic materials such as soot and fly ash (<3 %). Ammonium sulfate particles have rather uniform, submicron sizes (mostly 0.5 μm across). Sea-salt particles are larger, apparently having been deliquesced. However, submicron particles are also common. Many contain Na and mixed cation sulfates in addition to NaCl. Mineral dust consists largely of tabular clay particles. Samples from the July 28th flight contain much mineral dust, probably because of transport from the Saharan desert. Aggregates of sea salt and mineral dust, ammonium sulfate, and soot particles are common. Such mixed

aggregates are especially abundant in in-cloud samples. Cirrus samples from CRYSTAL-FACE contain many H_2SO_4 droplets, but acidic sulfate particles are rare at the cloud bases. H_2SO_4 probably formed at higher altitudes through oxidation of SO_2 in cloud droplets. Sea salt and mineral dust have been reported to be abundant in cloud particles collected using a counter-flow virtual impactor, suggesting that these particles were incorporated into the convective systems from the cloud bases and worked as ice nuclei while being vertically transported.

2. Kojima, T., Buseck, P.R., Wilson, J.C., Reeves, J.M., and Mahoney, M.J. (2004) Aerosol particles from tropical convective systems: Cloud tops and cirrus anvils. *Journal of Geophysical Research-Atmospheres* **109**, doi:10.1029/2003JD004504.

Aerosol particles from the upper troposphere (UT) and lower stratosphere (LS) were collected during the Cirrus Regional Study of Tropical Anvils and Cirrus Layers-Florida Area Cirrus Experiment (CRYSTAL-FACE) and studied by transmission electron microscopy (TEM). Samples were classified into three categories: (1) UT in-cloud, (2) UT out-of-cloud, and (3) LS. Sulfate particles, including former H_2SO_4 droplets, are dominant in samples from all categories. The morphology of H_2SO_4 droplets indicates that they had been ammoniated to some extent at the time of collection. They are internally mixed with organic materials, metal sulfates, and solid particles of various compositions. K- and S-bearing organic particles and Si-Al-rich particles are common to the three kinds of samples. In-cloud samples contain abundant Zn-rich particles. Their origin is unclear, but it seems likely that they are contaminants that originated through impact by ice cloud particles on the aircraft or sampling system. Ammoniation and internal mixing of H_2SO_4 in the UT aerosols may result in freezing at higher temperature than in pure H_2SO_4 aerosols. The relatively high extent of ammoniation in the UT in-cloud samples may have resulted from vertical transport of ammonia by strong convection. Abundances of nonsulfate particles decrease with increasing altitudes. The nonsulfate particles originated from the lower troposphere and were transported to the UT and LS.

3. Murphy, D.M., Cziczo, D.J., Hudson, P.K., Thomson, D.S., Wilson, J.C., Kojima, T., and Buseck, P.R. (2004) Particle generation and resuspension in aircraft inlets when flying in clouds. *Aerosol Science and Technology* **38**, 400-408.

Using on-line analysis of single particles, we have observed both generation and resuspension of particles when ice crystals, cloud droplets, or dust impact an aircraft inlet. Large numbers of particles smaller than $1\text{ }\mu\text{m}$ with a composition suggesting stainless steel were measured when flying a stainless steel inlet through cirrus clouds. Smaller numbers of metal particles were also observed when flying through dust or water clouds. A different instrument, sampling through a different inlet, found zinc particles when sampling in cirrus clouds. Laboratory experiments have verified that high-speed ice crystals can abrade stainless steel. Collision of ice crystals with the inlet wall also resuspended previously deposited particles. A notable example came when a flight through the space shuttle exhaust plume deposited large numbers of unique particles in our inlet. Some of the same types of particles were observed when the

aircraft flew into an ice cloud the following day. The generation of particles by impaction of ice crystals and dust in inlets may have affected some published results about ice nuclei and metal particles in the upper troposphere. The newly generated particles cannot be distinguished from atmospheric particles by size alone.

Abstracts of oral presentations

4. Buseck, P.R., Friedrich, H., Kojima, T., and Spinsby, J. (2004) Nanoparticles in the troposphere, 227th Am. Chem. Soc. Natl. Mtg., Anaheim, CA. *ACS Abstrs.*, Abstr. I&EC 40, March, 2004.

Tropospheric aerosol particles are ubiquitous, complex in composition and structure, and have important effects on solar radiation, climate, and human health. Using transmission electron microscopy (TEM), one can observe coatings and internal mixing (aggregation), which provide evidence of airborne reactions. Sulfate coatings are especially prominent on both soil and anthropogenic particles collected near Japan. Electron tomography with TEM permits obtaining of three-dimensional images of nanoparticles. We are using it to study soot (black carbon). Absorption of sunlight by soot aerosol particles is affected by their total mass, morphologies, and surface areas. The morphologies and surface areas change with time and have implications for the effectiveness of soot aerosols as global warming agents. Electron tomography offers a uniquely powerful way for studying details of such changes of aerosol nanoparticles as they aggregate and age.

5. Kojima, T., Buseck, P.R., and Reeves, J.M. (2003) Comparison of aerosol particles collected from cloud bases and cirrus anvils, Am. Geophys. Union Fall Mtg., San Francisco, CA. *Eos, Trans. AGU 84 (46)* Fall Meet. Suppl., Abstr. A12D-08, December, 2003.

Deep convection in tropical regions can vertically transport aerosol particles that potentially affect formation of cirrus clouds. In order to better understand the processes occurring in the convective clouds, we studied aerosol particles from cloud bases (altitudes: 1-3 km) and cirrus anvils (altitudes: 13-15 km) and compared their morphologies and compositions.

Aerosol sampling was performed during the July 2002 CRYSTAL-FACE mission. Particles between 0.07 and 3 μm were collected directly onto TEM grids. Cloud-base samples consist of ammonium sulfate (50-90 % by number), sea salt (5-35 %), Na- and Ca-sulfates (2-25 %), soil particles (2-15 %), and anthropogenic materials such as soot and flyash (< 3 %). These particles are similar in morphology to those from marine boundary layers. In contrast, cirrus samples have different particle types. They contain abundant (35-80 %) tiny round particles (0.05-0.5 μm) that appear to have been solution droplets. The particles are rich in S and O and contain elements such as Na, Mg, Cl, K, Ca, and Fe. Droplets of sulfuric acid (10-25 %) and Zn-rich particles (5-40 %) are also abundant in cirrus samples.

Direct links between aerosol particles from cloud bases and cirrus anvils are not evident. Hygroscopic ammonium sulfate and sea salt particles tend to develop into aqueous droplets that rapidly grow and are removed from convecting air mass by

precipitation. The remaining particles experience mixing, coagulation, and break-up in the clouds. The round S- and O-rich particles in the cirrus samples presumably formed through such complex processes.

6. Kojima, T., Buseck, P.R., Wilson, J.C., and Reeves, J.M. (2003) TEM analysis of aerosol particles and its application to cloud formation and climate, 2003 Symp. on "Recent Developments and Applications of Atomic Resolution Electron Microscopy and Spectroscopy - a Silver Jubilee," Tempe, AZ, ASU. *Prog. & Abstr.*, January, 2003.

Aerosol particles can be precursors of ice crystals or water droplets in clouds, and thus have significant influences on local and global climate. Individual particle analysis by TEM reveals their chemical compositions, morphologies, sizes, and crystal structure. These factors are important in discussing formation and evolution of cloud particles.

Here we present the results of our study of aerosol particles collected during a recent field campaign in Key West, Florida. Aerosol samples from the lower stratosphere (~17 km high), the upper troposphere (~14 km high), and cloud bases (~1 km high) were analyzed. We compare their characteristics and discuss how particles affect cloud formation.

7. Kojima, T., Buseck, P.R., Wilson, J.C., and Reeves, J.M. (2002) Aerosol particles from tropical cirrus clouds in the lower stratosphere: Am. Geophys. Union Fall Mtg., San Francisco, CA. *Eos, Trans. AGU 83 (47)* Fall Meet. Suppl., F106, Abstr. A71F-06, December, 2002.

Aerosol samples were collected from convective systems and cirrus layers over Florida during the July 2002 CRYSTAL-FACE Mission. Particles between 0.02 and 700 μm were deposited directly onto TEM grids. Here we report preliminary results of the TEM study of particles collected near and above the tropopause.

Most particles are sulfate droplets that range from 0.8 to 5 μm in diameter on the TEM grids. All have a characteristic appearance that consists of a main central particle (0.3 -1 μm) surrounded by many smaller satellite droplets. Their appearance suggests that the droplets were sulfuric acid partially neutralized with ammonium at the time of collection, with ammonium sulfate and bisulfate constituting the central particles. The degree of ammoniation in individual droplets, which is indicated by the size of central particles relative to satellite ring diameter, is fairly uniform. The ratio of central particle diameter to satellite ring diameter is generally around 0.3. Such ammoniated droplets with solid cores may be more efficient in nucleating cirrus than pure sulfuric acid droplets. Ammonium sulfate particles without satellites commonly coexist with the acid droplets.

Minor particles consist of C-rich amorphous material, silicates, Na- and K-chlorides and sulfates, and Cr- and Ti-oxides. Some were coated with sulfate. Many of the C-rich particles contain significant amount of K, S, and O with lesser N. All silicate particles are flakes of clay minerals that have pseudohexagonal structures. They would work as effective ice nuclei.